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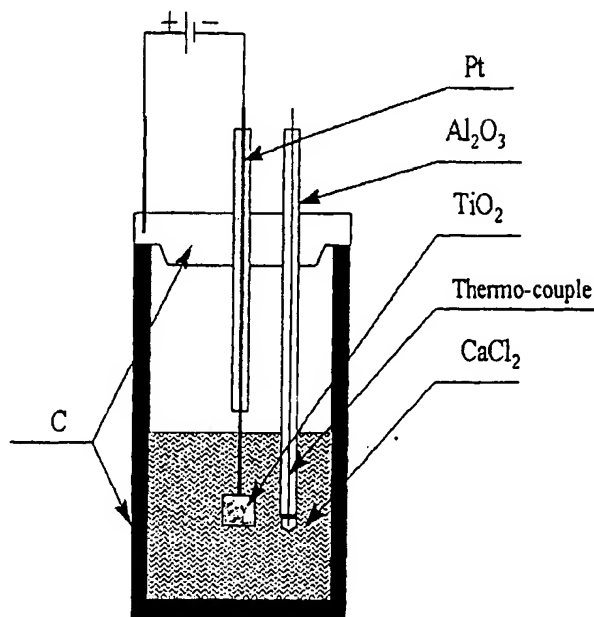
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[Continued on next page]

(54) Title: EXTRACTION OF METALS



Schematic of the experimental set up

(57) Abstract: A method of producing a metal or an alloy from metalliferous material by removing O, S, or N from a solid body of metalliferous material by electrolysis in an electrolytic cell is disclosed. The cell includes a molten halide salt or mixture of halide salts as an electrolyte. The cation of the salt is selected from the group that includes Ca, Ba, Li, Na, K, Mg, Sr, Cs and Y. In one aspect of the invention the method includes conducting the electrolysis under conditions wherein the solid body of metalliferous material is made part of a cathode of the electrolytic cell, the cathode includes a conductor for electrically connecting the cathode with an electrical potential, the conductor has high resistance to chemical attack by the electrolyte at high temperatures, and the conductor is at least partly immersed in the electrolyte. In another aspect of the invention the method includes conducting the electrolysis under conditions wherein the potential applied between an anode and the cathode of the electrolytic cell is chosen such that permanent decomposition of the electrolyte is avoided to an extent that substantial deposition of the electrolyte cation at the cathode is avoided and anode material transport towards and into the cathode is substantially prevented. A cathode for use in the method is also disclosed. The cathode includes a body of metalliferous material distributed around one or more electrical conductors that are substantially inert in the electrolyte

at high temperatures and which provide a plurality of reduction zones at the cathode.

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Extraction of Metals

Field of Invention

5 The present invention relates to methods of producing metals from metalliferous materials such as metal oxides.

Background of the Invention

10

 It is well known to produce metals from metalliferous ores by a methods that include the steps of: 1) concentrating an ore; 2) reducing the ore concentrate under high temperature conditions in the presence of a
15 suitable reductant and producing a crude metal; and 3) refining the crude metal.

 The present invention is concerned with alternative methods of producing metals from metalliferous
20 materials that are based on the use of electrochemical cells.

Prior Art

25 A. A paper entitled "Electrochemical deoxidation of titanium" published in Metallurgical Transactions B, Volume 24B, June 1993, pages 449-445 (Authors: TH Okabe, M Nakamura, T Oishi and K Ono).

30 The Okabe et al paper discloses an electrochemical method of removing oxygen dissolved in titanium.

 The paper reports experimental work on an
35 electrolytic cell that included a cathode of titanium having up to 1400ppm dissolved oxygen and an anode of graphite. The cathode and the anode were immersed in a

- 2 -

molten CaCl_2 electrolyte bath. Electrical potentials between 0 and 6V were applied between the anode and the cathode. CaCl_2 was employed to produce calcium and to facilitate the calcium reaction by decreasing the activity of the electrolytic by-product CaO . The calcium potential in CaCl_2 was increased at the titanium cathode surface as a result of the application of the electrical potential across the anode and the cathode. This resulted in deoxidisation of the cathode by the electrolytically produced calcium or by calcium of high activity in the CaCl_2 . The resulting oxygen ions, which were mainly present in the deoxidisation product in the electrolyte, reacted at the graphite anode to form CO or CO_2 gas that was removed from the system.

15

B. A paper entitled "Electrochemical deoxidation of yttrium-oxygen solid solutions" published in Journal of Alloys and Compounds, Volume 237, 15 April 1996, pages 150-154 (Authors: T H Okabe, T N Deura, T Oishi, K Ono and D R Sadoway).

20

The Okabe et al paper discloses an electrochemical method of removing oxygen dissolved in yttrium.

25

The paper describes experimental work on solid yttrium containing dissolved oxygen. The yttrium was placed in a titanium basket cathode and thereafter immersed in a bath of molten CaCl_2 electrolyte. The CaCl_2 electrolyte bath was contained in a titanium crucible and a constant voltage of between 3.2 to 3.8V was applied between the cathode and a graphite anode submerged in the electrolyte. Electrolysis was carried out at 1223K (950°C) for a specified time.

30

C. International application PCT/GB99/01781 (patent publication WO99/64638) (Fray et al).

35

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The Fray et al International application discloses two potential applications of a "discovery" in the field of metallurgical electrochemistry.

5

One application is the direct production of metal from a metal oxide.

10 The other application is the removal of impurities that are "dissolved" in a solid metal. The same basic process is said to be applicable to both applications.

15 The "discovery" is the realisation that an electrochemical method can be used to ionise oxygen contained in a solid metal so that the oxygen dissolves in an electrolyte", compare page 5, lines 14-16. The International application discloses that when a suitably negative potential is applied in an electrochemical cell
20 with an oxygen-containing metal as a cathode, a reaction occurs whereby oxygen is ionised and is subsequently able to dissolve in the electrolyte of the cell.

The International application discloses an
25 electrolytic cell that includes a body of a metalliferous material (such as a metal oxide in which impurities are dissolved) as a cathode of the cell. The cathode is immersed in a molten bath of a suitable electrolyte. A predetermined electrical potential that is lower than the
30 decomposition potential of the electrolyte is applied between the cathode and a suitable anode (either a separate graphite anode or the electrolyte crucible). The potential is chosen such that it has a value that allows a selected impurity (i.e. O, S, C or N) to be ionised and
35 thus diffuse through the body of metalliferous material into the electrolyte where it dissolves.

- 4 -

The International application lists a substantial number of metals that are said to be susceptible for use in the above-described method. These metals are titanium (Ti), silicon (Si), germanium (Ge), zirconium (Zr),
5 hafnium (Hf), samarium (Sm), uranium (U), aluminium (Al), magnesium (Mg), neodymium (Nd), molybdenum (Mo), chromium (Cr), niobium (Nb) or any alloys thereof.

All of the examples in the International
10 application relate to the "purification" and/or reduction of titanium, titania, and specific titanium/aluminium alloys, namely Ti6Al4V, compare pages 9-14 of the International application. Example 12 relates to the creation of a Ti-Al alloy starting from a mixture of TiO₂
15 and Al₂O₃. The ranges of applied voltage in the different examples varied from as low as 1.75V (see example 2) to 3.3V (compare example 3). Most experiments were conducted at a controlled voltage of 3.0V. Process times varied. Crucibles used were made from alumina, graphite, or
20 titanium whereby the anode was either the crucible or a separate graphite rod. The only electrolyte used in all of the examples was CaCl₂.

Summary of Invention

25

Experimental work was carried out at the Minerals Technology Centre, Newcastle Laboratories, of the applicant to reproduce the experiments carried out the above-referenced prior art documents.

30

The experimental work resulted in the following findings and inventions.

1. Titanium of very low oxygen concentration could
35 be produced directly from titania by electrolysis in molten CaCl₂.

- 5 -

However, cell modification was required to reduce titania in an electrolytic cell, as the Fray et al International application in particular is silent on how to set up an electrolytic cell in order to achieve
5 reduction of a good electrical insulator such as titania. Reduction of titania could not be achieved within required parameters by following the experimental set-up disclosed in the Fray et al International application.

10 Accordingly, a first aspect of the invention is based on the realisation that the type of cathode leads in electrical contact with TiO_2 and CaCl_2 electrolyte severely influence the titania reduction process. While there is only a preliminary understanding of the mechanism, it is
15 likely that proper selection of the material and the type of electrical contact will be an important part of the electrolytic cell design specific to metal oxide to be reduced and the electrolyte employed therefor.

20 Accordingly, the first aspect of the invention is a method of producing a metal or an alloy from metalliferous material by removing an impurity (I) selected from the group including O, S, or N from a solid body of metalliferous material by electrolysis in an
25 electrolytic cell that includes molten halide salt or mixture of halide salts as an electrolyte, wherein the cation of said salt is selected from the group that includes Ca, Ba, Li, Na, K, Mg, Sr, Cs and Y, which method includes conducting the electrolysis under conditions
30 wherein:

(a) the potential applied between an anode and a cathode of the electrolytic cell is chosen such that permanent decomposition of
35 the electrolyte is avoided to an extent that substantial deposition of the electrolyte cation at the cathode is

- 6 -

avoided; and

5 (b) the body is made part of the cathode of the electrolytic cell, the cathode includes a conductor for electrically connecting the cathode with an electrical potential, the conductor has high resistance to chemical attack by the electrolyte at high temperatures, and the conductor is at least partly immersed in the electrolyte; and

10 (c) O, S, or N is removed from the cathode and passes into solution and/or chemically reacts with the electrolyte cation.

15 The metalliferous material may contain an oxide, sulfide, carbide or nitride of said metal.

20 Preferably the metalliferous material is a titanium-containing material.

Preferably the impurity is oxygen.

25 Preferably the titanium-containing material is titania.

Preferably the anode is formed from graphite.

30 Preferably the electrolyte is CaCl_2 .

2. Carbon was detected in reduced metal pellets produced in the experiments.

35 While the source of the carbon was the carbon anode employed in the experiments, the mechanism by which carbon found its way into the reduced metal is not fully understood. The absolute levels of carbon in some spots

- 7 -

of the metal pellet were too high to ignore.

Accordingly, in a second aspect of the invention there is provided a method of producing a metal or an alloy from metalliferous material by removing an impurity (I) selected from the group including O, S, or N from a solid body of metalliferous material by electrolysis in an electrolytic cell that includes molten halide salt or mixture of halide salts as an electrolyte, wherein the cation of said salt is selected from the group that includes Ca, Ba, Li, Na, K, Mg, Sr, Cs and Y, which method includes conducting the electrolysis under conditions wherein:

- (a) the potential applied between an anode and a cathode of the electrolytic cell is chosen such that permanent decomposition of the electrolyte is avoided to an extent that substantial deposition of the electrolyte cation at the cathode is avoided and anode material transport towards and into the cathode is substantially prevented;
- (b) the body is made part of the cathode of the electrolytic cell; and
- (c) O, S, or N is removed from the cathode and passes into solution and/or chemically reacts with the electrolyte cation.

Preferably the cathode includes a conductor having high resistance to chemical attack by the electrolyte at high temperatures for connecting the cathode with an electrical potential and the conductor is at least partly immersed in the electrolyte.

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The metalliferous material may contain an oxide, sulfide, carbide or nitride of said metal.

5 Preferably the metalliferous material is a titanium-containing material.

Preferably the impurity is oxygen.

10 Preferably the titanium-containing material is titania.

Preferably the anode is formed from graphite.

15 Preferably the electrolyte is CaCl_2 .

3. In using the above-described inventive methods, it was confirmed that Al_2O_3 in contact with a TiO_2 pellet body can be reduced and forms alloys with the reduced titanium.

20 4. It was found that silicon could be reduced from SiO_2 by electrolysis in molten CaCl_2 when employing the above-described methods. However, chlorine evolution in the case of SiO_2 reduction was observed to a higher degree
25 compared to TiO_2 reduction.

5. Reduction of Al from Al_2O_3 pellets by the above-described method was also attempted.

30 It was observed that reduction to Al took place only around the site of contact between the pellet and the electric leads connecting the cathode to the potential source. The portion of the pellet away from the cathode leads was not reduced at all.

35 This observation again suggests that the electrical conductivity of the cathode was a factor that

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affected the reduction process.

Accordingly, in another aspect of the invention, there is provided a cathode for use in the above described methods, wherein the cathode includes the body of metalliferous material distributed around one or more electrical conductors that are substantially inert in the electrolyte at high temperatures and which provide a plurality of reduction zones at the cathode.

6. The mechanisms of removal of oxygen from titanium, titania, yttrium and aluminium-titanium alloys suggested by the Fray et al International application and the Okabe et al papers using the electrolytic methods described are far from clear at present. The Fray et al International application suggests that the mechanism disclosed in the Okabe papers is incorrect. It is believed that both mechanisms are speculative insofar as other metals and oxides are concerned. Also, while there is evidence that the type of electrolyte influences the process parameters, its properties and role in the presented mechanisms is vague and only qualitative.

Experimental Data for the Inventions

A. Reduction of Titania

I. First Experiment

The purpose of the first experiment was to confirm (or otherwise) the feasibility of producing metallic titanium from titania by direct electrochemical reduction in molten CaCl_2 .

Specifically, the purpose of the first experiment was to confirm (or otherwise) the set-up described in the Fray et al International application.

- 10 -

Accordingly, the conditions of the experiment were kept as close as possible to the conditions in the examples of the International application.

5 The underlying principle of the process,
according to the Fray et al International application, is
based on ionisation of oxygen in an oxide as a result of
applying suitable negative potential to it in
10 electrochemical cell and subsequent dissolution in the
electrolyte.

II. Experimental Method and Equipment

15 The experimental set-up is shown in Figure 1.

With reference to Figure 1, the electrochemical
cell included a graphite crucible equipped with a graphite
lid. The crucible was used as the cell anode. A stainless
steel rod was used to secure electrical contact between a
20 d/c power supply and the crucible. The cell cathode
consisted of Kanthal or platinum wire connected at one end
to the power supply and TiO_2 pellets suspended from the
other end of the wire. An alumina tube was used as an
insulator around the cathode.

25 A type B thermocouple, contained in an alumina
sheath, was immersed in the electrolyte in close proximity
to the pellets.

30 Two types of pellets were used. One type was
slip-cast and the other type was pressed. Both types of
pellets were made from analytical grade TiO_2 powder. Both
types of pellets were sintered in air at 850°C . One
pressed and one slip-cast pellet were used in the
35 experiment.

The experiment was conducted at 950°C . Voltages

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up to 3V were applied between the crucible wall and the Kanthal or platinum wire.

5 The power-supply maintained a constant voltage throughout the experiment. The voltage and resulting cell current were logged using LabVIEW (TM) data acquisition software.

10 III. Experimental Results

With reference to Figures 2 and 3, the constant voltage (3V) used in the experiment produced an initial current of approximately 1.2A. A continuous drop in the current was observed during the initial 2 hours. After 15 that a gradual increase in the current up to 1A was observed.

At the end of the experiment the cell was removed from the furnace and quenched in water. The solid 20 CaCl_2 was dissolved by water and the two pellets were recovered.

SEM images of the cross-sections of the two pellets are shown in Figures 4 and 5.

25 The presence of virtually pure metallic titanium in both pellets was confirmed by EPMA analysis. The analysis also showed areas of partially reduced titania. The EPMA results are shown in Figures 6 and 7.

30 Carbon was detected at various locations within the pellets and its content varied up to 18wt%.

35 B. Reduction of Silicon

I. Experimental Method and Equipment

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The experimental set-up was essentially the same as in the case of titanium. The cathode consisted of platinum-rhodium wire and SiO_2 pellets suspended from the end of the wire.

5

The experiment was conducted at 950°C .

II. Experimental Results

10 The voltage used in the experiment was 3V, which produced initial current of approximately 1.5A as shown in Figure 8. After that a gradual decrease in the current to 0.65A was observed.

15 The working potential was selected as 3V in order to overcome resistance and overvoltage. However, chlorine liberation was observed at 3V although it is below the theoretical decomposition potential of CaCl_2 , which is 3.25V at 950°C .

20

The experiment was terminated after 4 hours. The partially reduced pellets were isolated by dissolution of the CaCl_2 in water. The surface and interior of the samples were analysed by SEM.

25

Analysis of the surface of the pellets showed the presence of some oxygen, indicating that there was partial reduction only in these regions.

30 However, the oxygen concentration in these regions was much lower than the oxygen concentration in SiO_2 - as is shown in Figure 9.

35 The structure of the partially reduced regions of the pellets is shown in Figure 10. Regions of different phases, such as SiO_2 and $2\text{CaO}.\text{SiO}_2$, were detected - see Figures 11 to 13.

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Pure unreduced SiO_2 was present in the centre of the pellets.

5 Pure Si was identified in the proximity of the platinum leads - as shown in Figures 14 to 17.

10 Many modifications may be made to the inventions as described above without departing from the spirit and scope of the inventions.

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CLAIMS:

1. A method of producing a metal or an alloy from metalliferous material by removing an impurity (I)
5 selected from the group including O, S, or N from a solid body of metalliferous material by electrolysis in an electrolytic cell that includes molten halide salt or mixture of halide salts as an electrolyte, wherein the cation of said salt is selected from the group that
10 includes Ca, Ba, Li, Na, K, Mg, Sr, Cs and Y, which method includes conducting the electrolysis under conditions wherein:
- (a) the potential applied between an anode and
15 a cathode of the electrolytic cell is chosen such that permanent decomposition of the electrolyte is avoided to an extent that substantial deposition of the electrolyte cation at the cathode is
20 avoided; and
- (b) the body is made part of the cathode of the electrolytic cell, the cathode includes a
25 conductor for electrically connecting the cathode with an electrical potential, the conductor has high resistance to chemical attack by the electrolyte at high temperatures, and the conductor is at least partly immersed in the electrolyte; and
- 30 (c) O, S, or N is removed from the cathode and passes into solution and/or chemically reacts with the electrolyte cation.
- 35 2. The method defined in claim 1 wherein the metalliferous material contains an oxide, sulfide, carbide or nitride of said metal.

- 15 -

3. The method defined in claim 1 or claim 2 wherein the metalliferous material is a titanium-containing material.

5

4. The method defined in claim 3 wherein the titanium-containing material is titania.

5. The method defined in any one of the preceding claims wherein the impurity is oxygen.

10

6. The method defined in any one of the preceding claims wherein the anode is formed from graphite.

7. A method of producing a metal or an alloy from metalliferous material by removing an impurity (I) selected from the group including O, S, or N from a solid body of metalliferous material by electrolysis in an electrolytic cell that includes molten halide salt or mixture of halide salts as an electrolyte, wherein the cation of said salt is selected from the group that includes Ca, Ba, Li, Na, K, Mg, Sr, Cs and Y, which method includes conducting the electrolysis under conditions wherein:

15
20
25

(a) the potential applied between an anode and a cathode of the electrolytic cell is chosen such that permanent decomposition of the electrolyte is avoided to an extent that substantial deposition of the electrolyte cation at the cathode is avoided and anode material transport towards and into the cathode is substantially prevented;

30

35

(b) the body is made part of the cathode of the electrolytic cell; and

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(c) O, S, C or N is removed from the cathode and passes into solution and/or chemically reacts with the electrolyte cation.

5

8. The method defined in claim 7 wherein the cathode includes a conductor having high resistance to chemical attack by the electrolyte at high temperatures for connecting the cathode with an electrical potential and the conductor is at least partly immersed in the electrolyte.

9. The method defined in claim 7 or claim 8 wherein the metalliferous material contains an oxide, sulfide, carbide or nitride of said metal.

10. The method defined in any one of claims 8 to 9 wherein the metalliferous material is a titanium-containing material.

20

11. The method defined in claim 10 wherein the titanium-containing material is titania.

12. The method defined in any one of claims 7 to 11 wherein the impurity is oxygen.

13. The method defined in any one of claims 7 to 12 wherein the anode is formed from graphite.

14. A cathode for use in the method defined in any one of the preceding claims includes the body of metalliferous material distributed around one or more electrical conductors that are substantially inert in the electrolyte at high temperatures and which provide a plurality of reduction zones at the cathode.

35

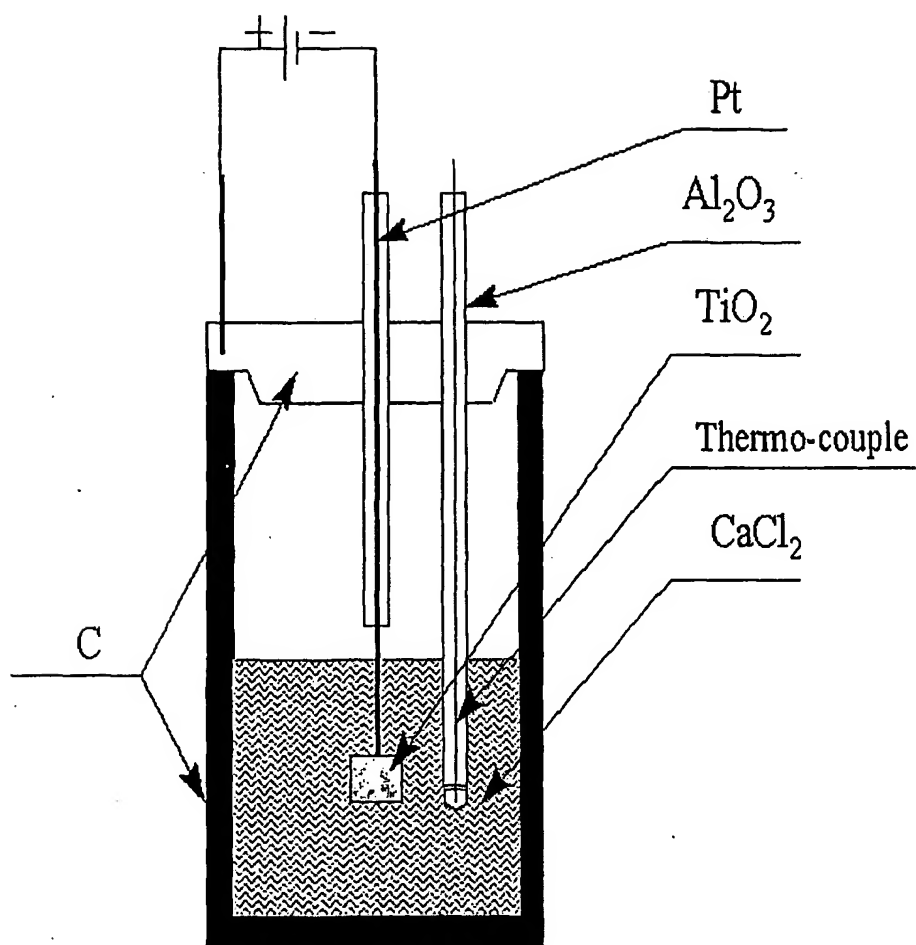


Fig. 1 Schematic of the experimental set up

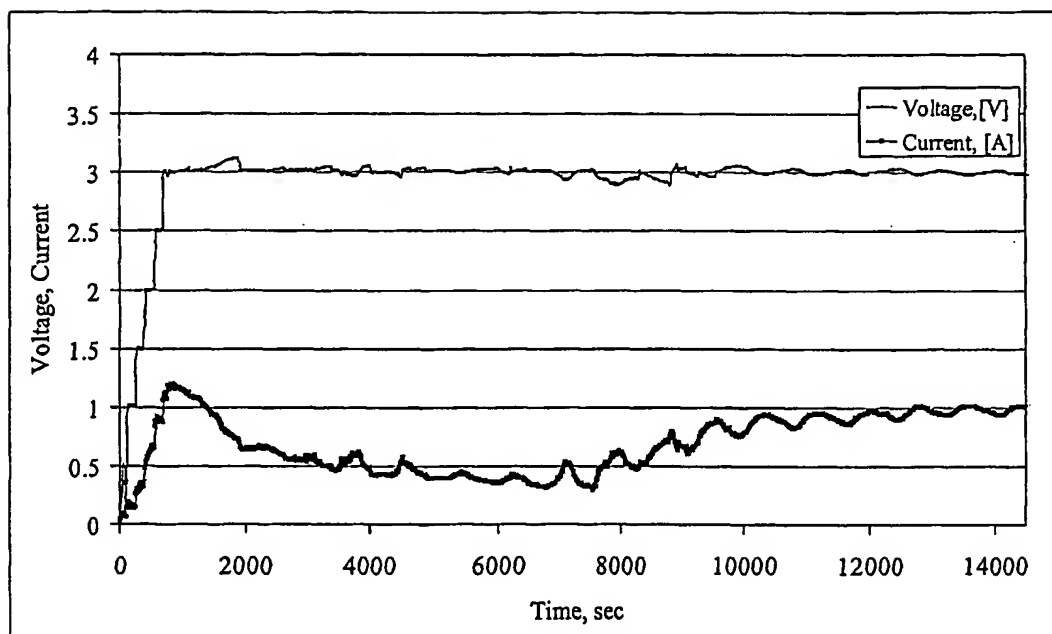


Fig 2. Variation of the applied potential and current during the run

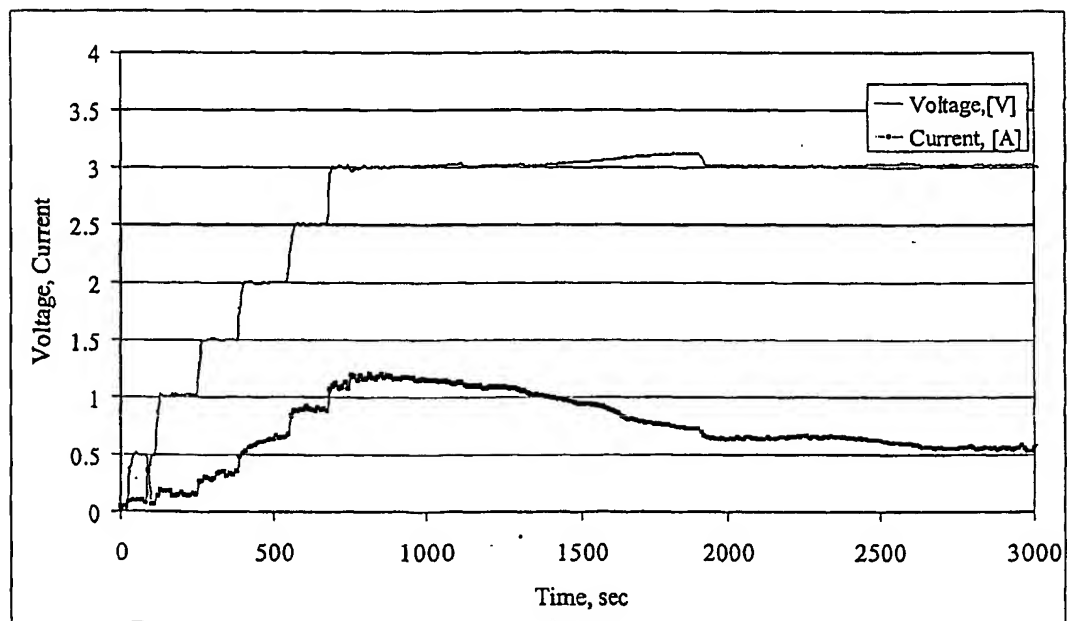


Fig 3. Variation of the applied potential and current in the initial stage of the run

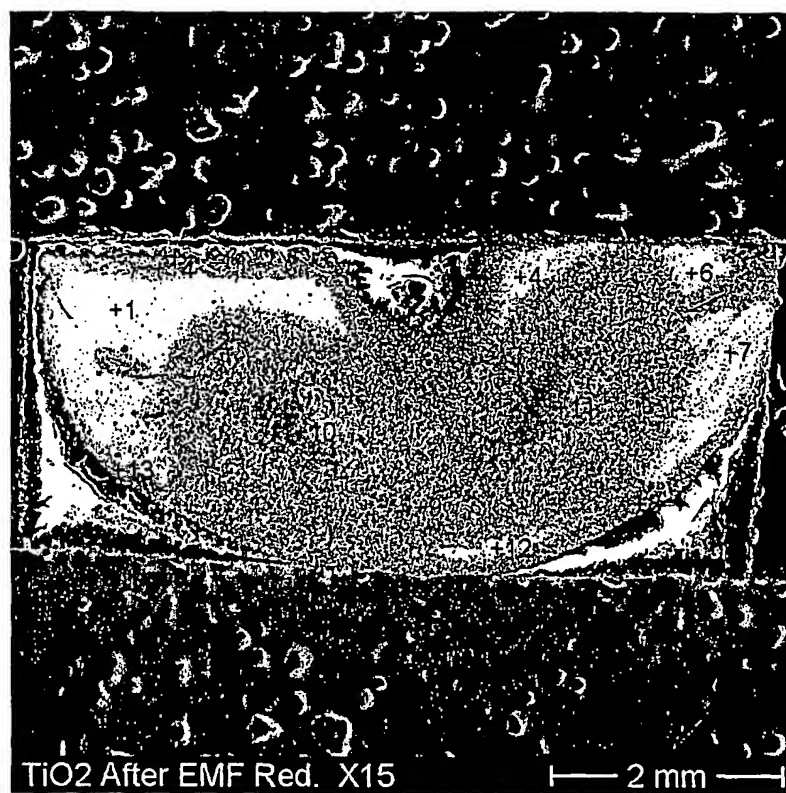


Fig 4. SEM image of the horizontal cross-section of Pellet 1 after the run

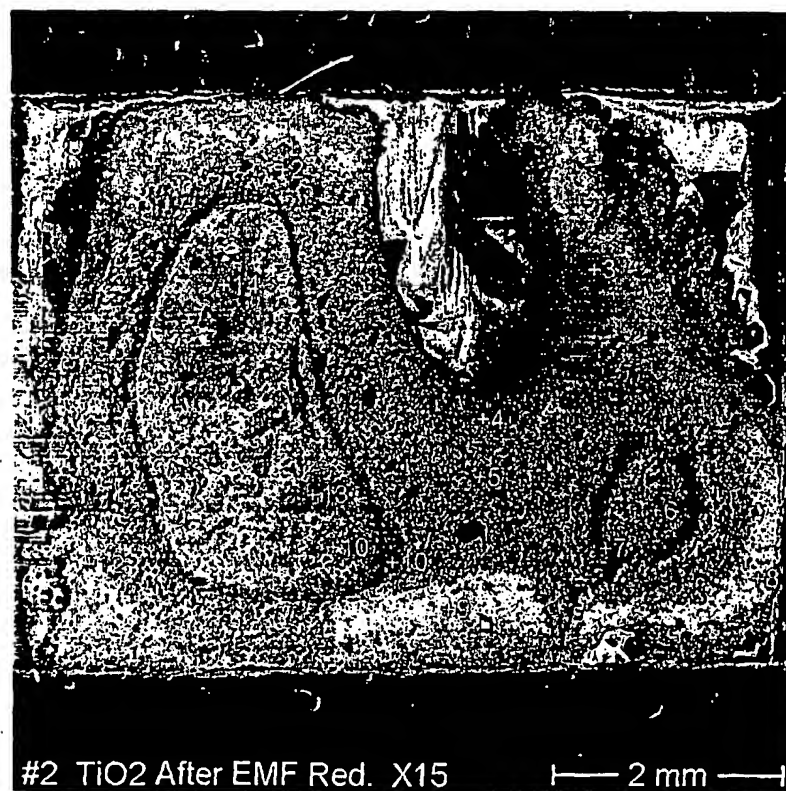


Fig. 5. SEM image of a horizontal cross-section of Pellet 2 after the run

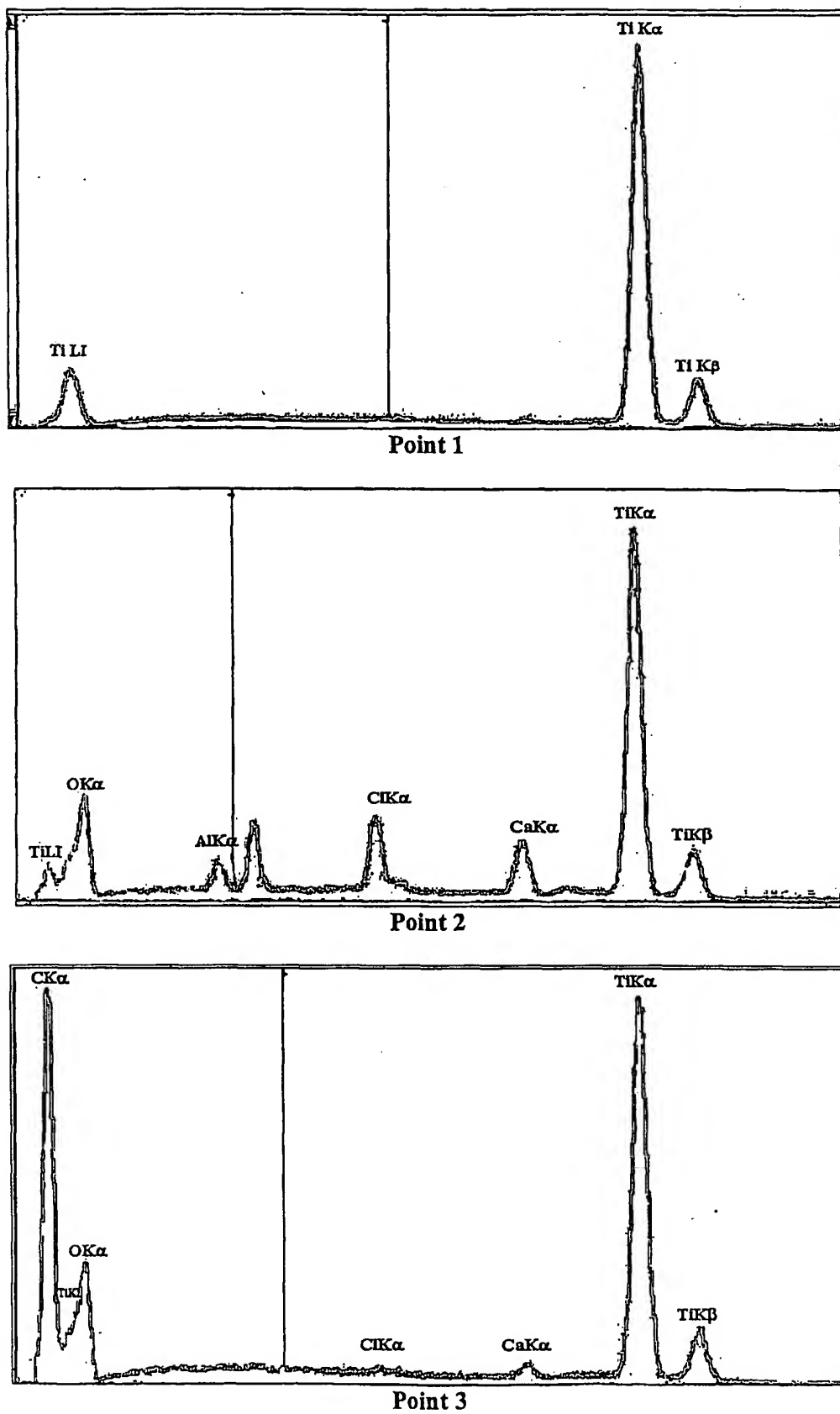
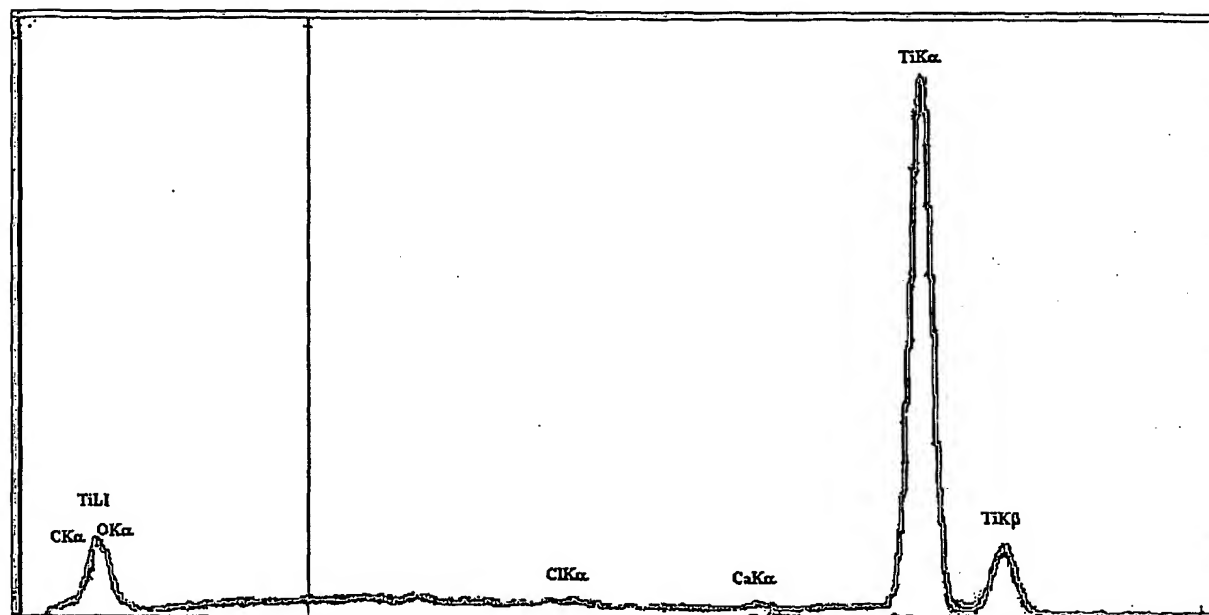
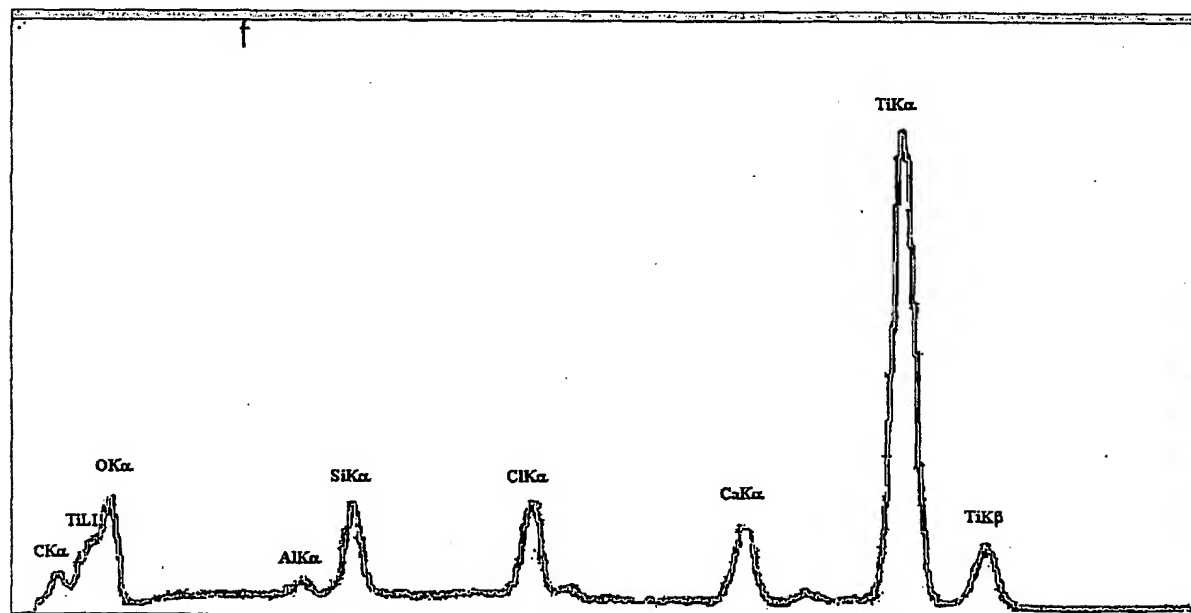


Fig. 6. EPMA analysis of Pellet 1 (Pressed)

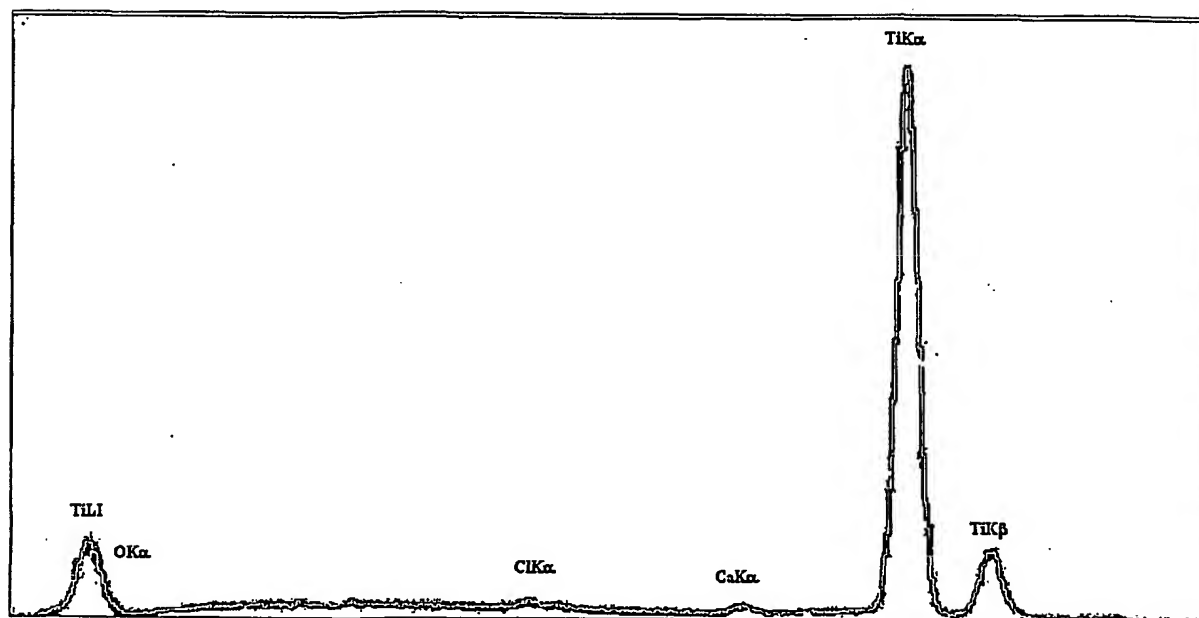


Point 1

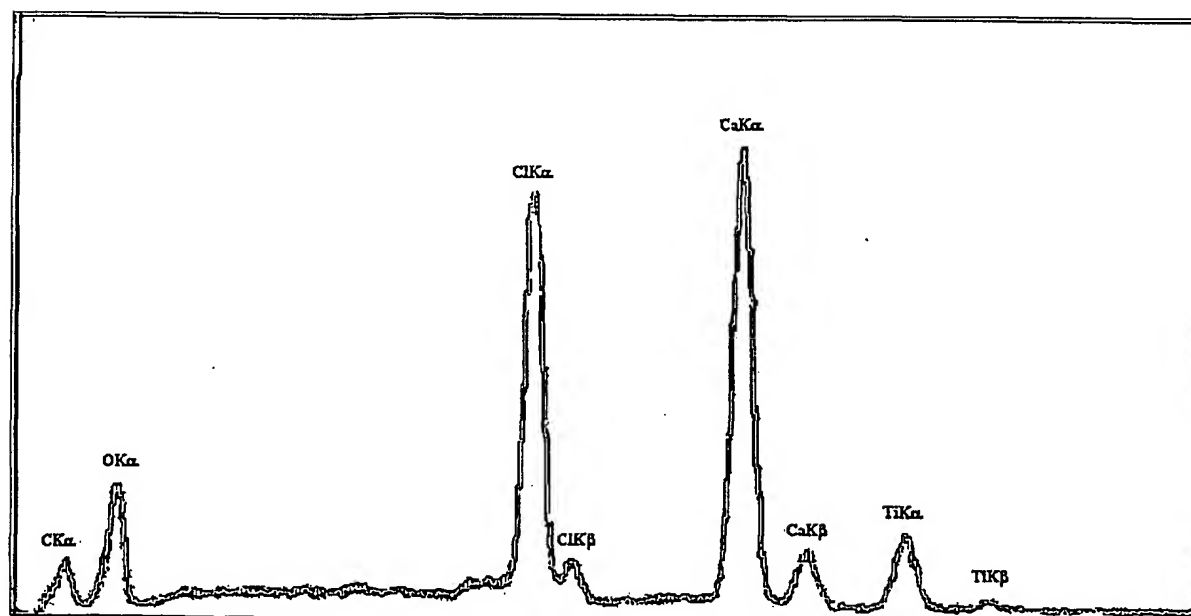


Point 2

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) – Part 1



Point 3



Point 14

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) – Part 2

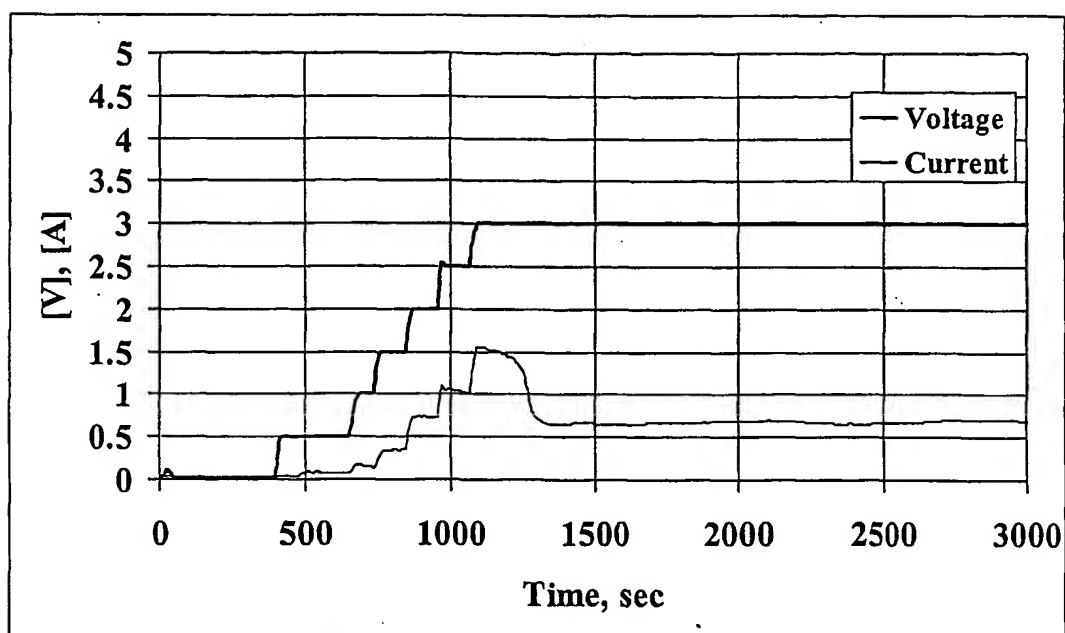


Fig. 8. Variation of the applied potential and current in the initial stage of the run

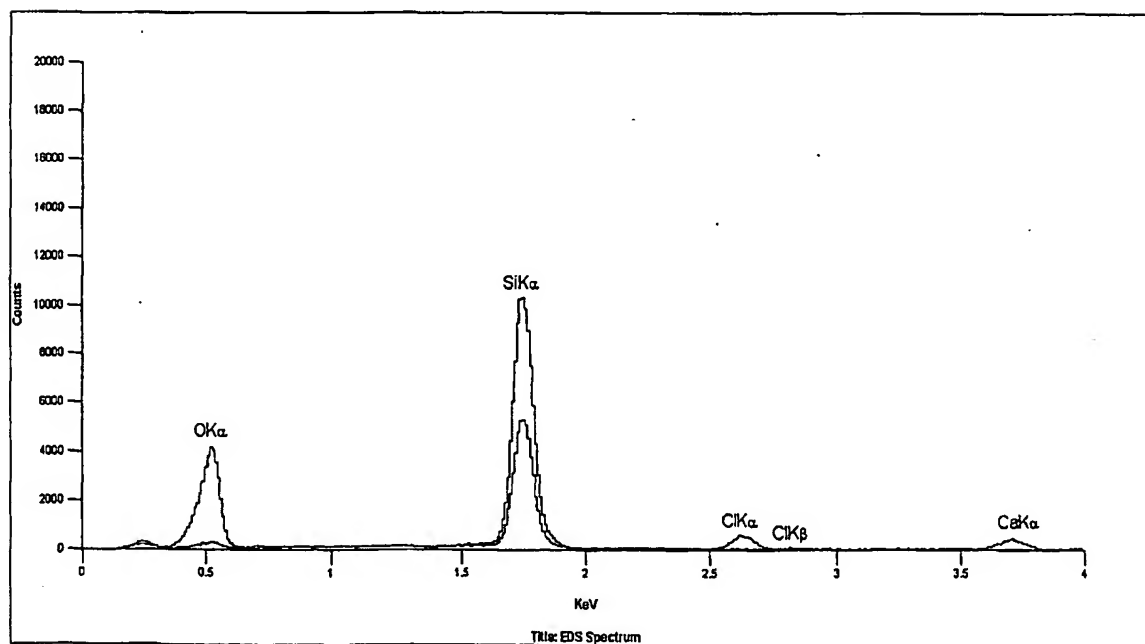


Fig. 9. Comparison of the spectrum of pure SiO_2 with the one of the surface of the sample after reduction



Fig. 10. Appearance of the structure of the SiO₂ pellet after reduction

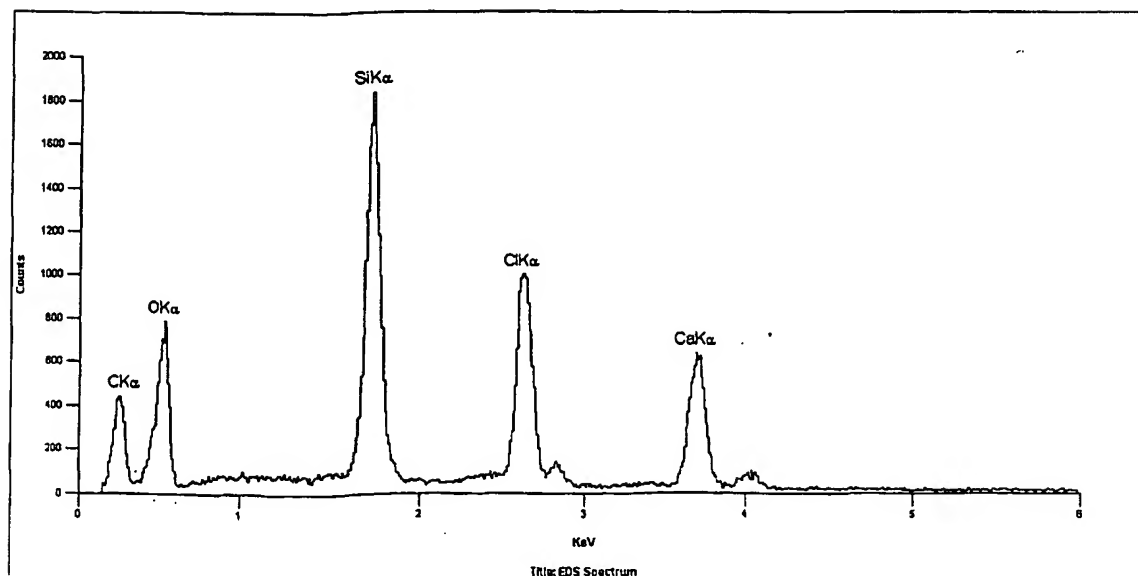


Fig. 11. Spectrum at point 8 in Figure 10.

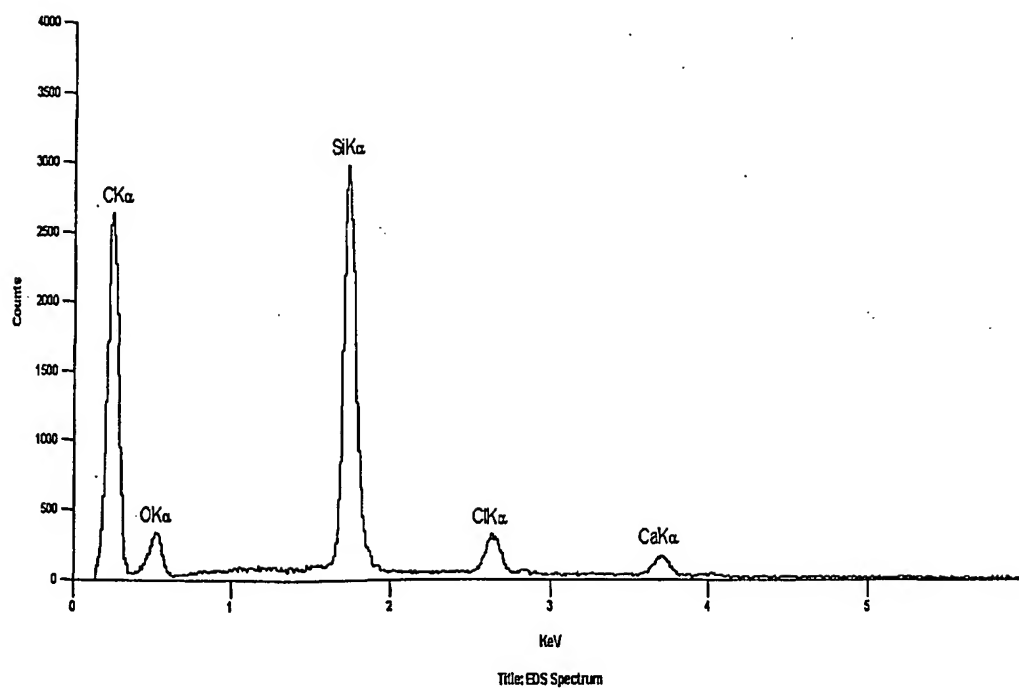


Fig. 12. Spectrum at point 10 in Figure 10.

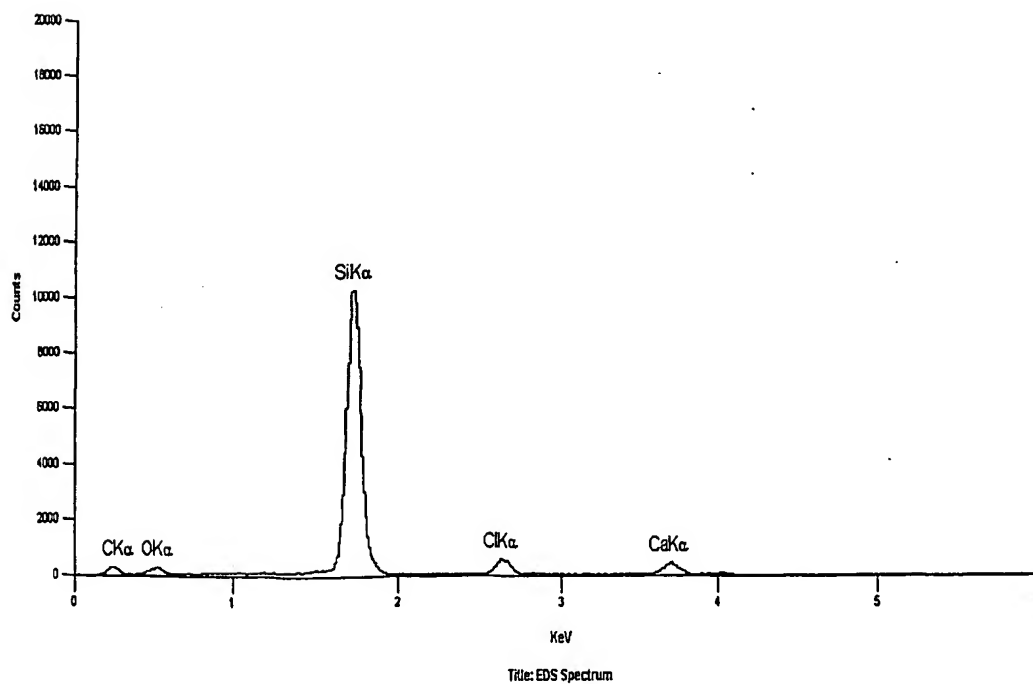


Fig. 13. Spectrum at point 10 in Figure 10.

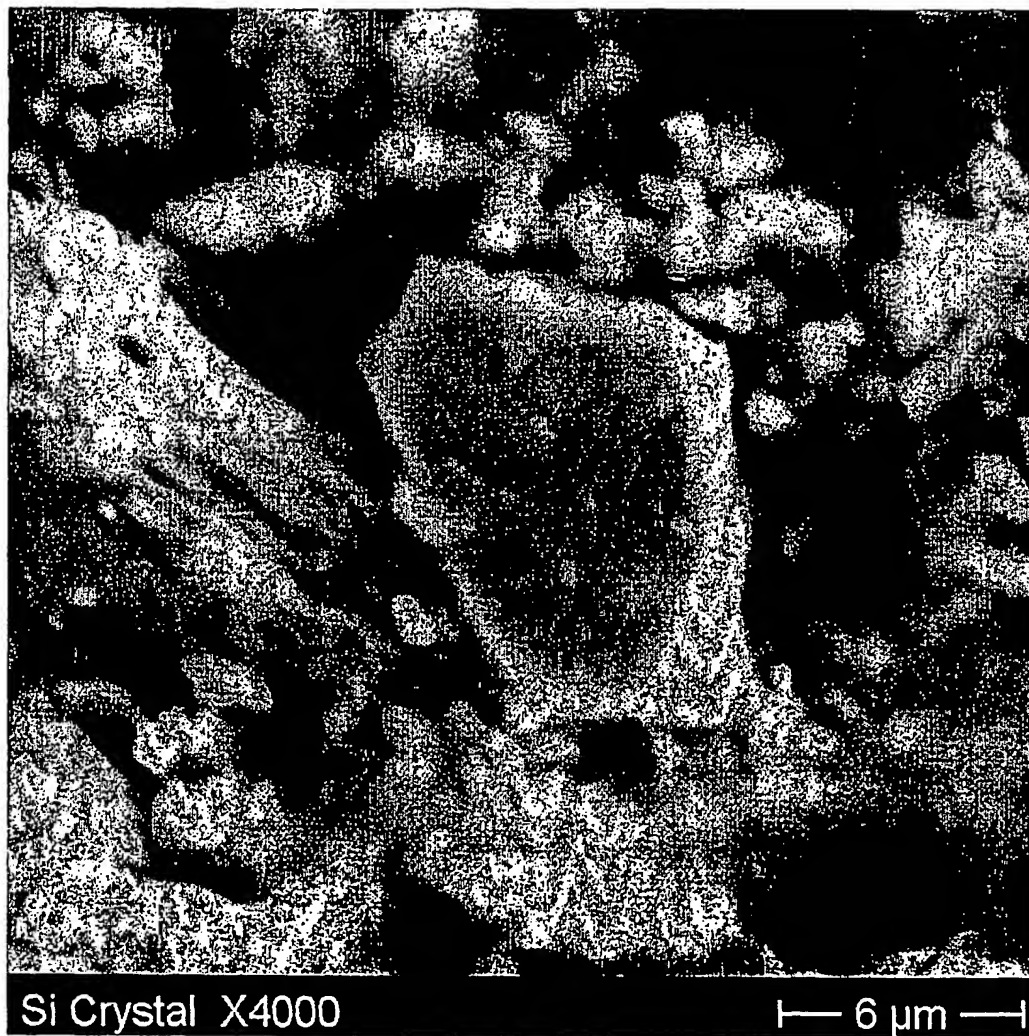


Fig. 14. Silicon crystal found in the pellet after reduction

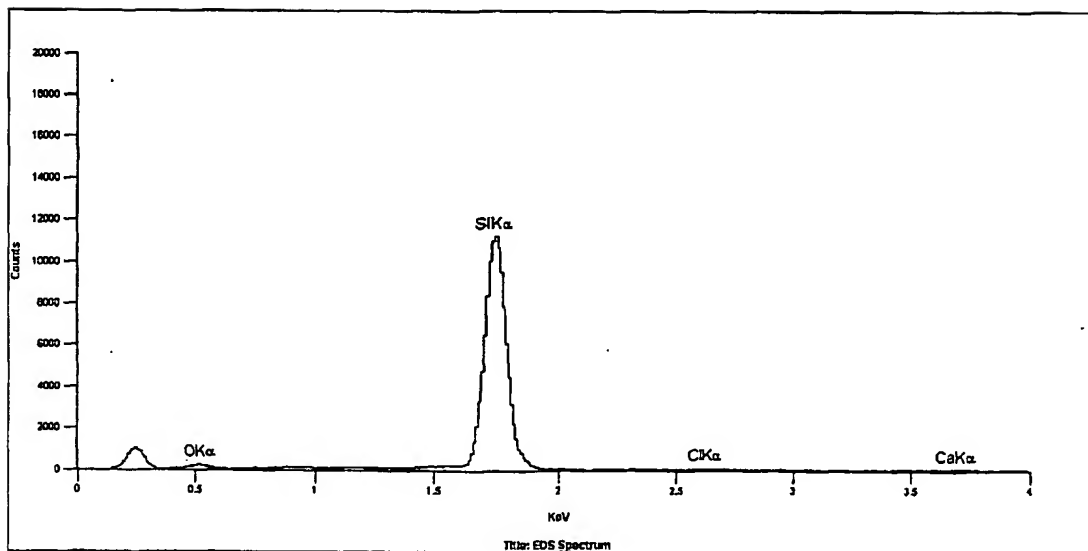


Fig. 15. Spectrum of the crystal in Figure 14.

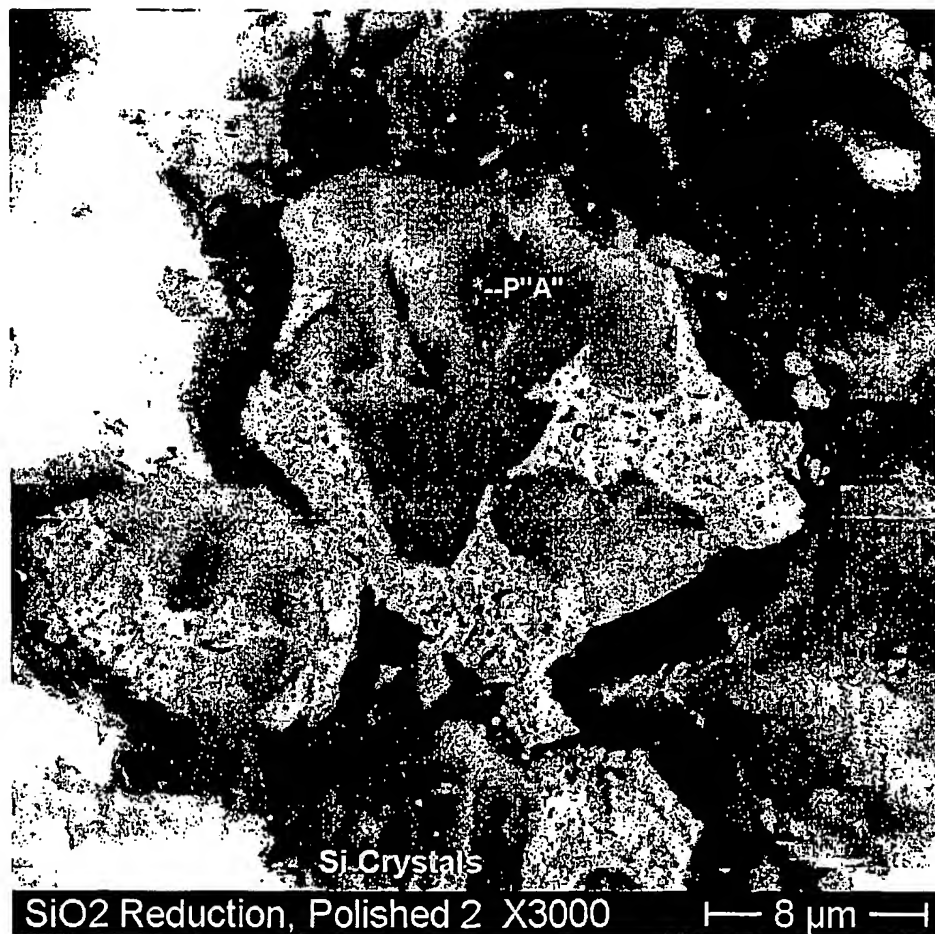


Fig. 16. Silicon crystal found in the pellet after reduction

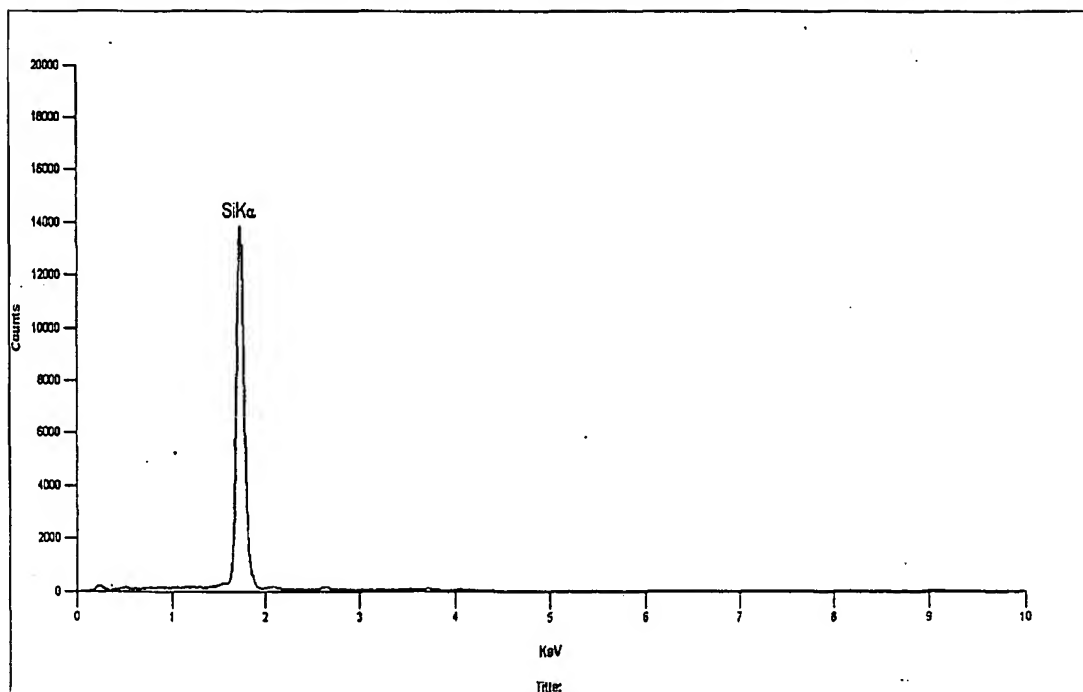


Fig. 17. Spectrum at point A in Figure 16.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00168

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: C25C 5/00, C22B9/14, 34/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC⁷ AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practicable, search terms used)
Derwent WPAT: IPC⁷ as above and electrol+**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9964638 A1 (Cambridge University Tech Serv Ltd) 16 December 1999 Whole Document	1 to 14
A	GB 2359564 A (Secretary of State for Defence UK) 29 August 2001 Whole Document	

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Date of the actual completion of the international search
13 March 2002Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU02/00168

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Patent Document Cited in Search Report				Patent Family Member			
WO 9964638	AU 42770/99	BR 9910939	CZ 20004476				
	EP 1088113	HU 200102934	NO 20006154				
	PL 344678						
GB 2359564	AU 200133871	AU 200133876	AU 200133890				
	WO 200162994	WO 200162995	WO 200162996				
	GB 2362164						
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